STUDY OF DIFFUSION COEFFICIENTS OF GLASSES UNDER ZERO-G

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DIFFUSION COEFFICIENTS OF GLASSES UNDER ZERO-G

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February 5, 1975

This report outlines the work conducted under NASA/MSFC contract NAS8-30656 during the initial six months period and indicates the direction of the next year of work on that contract. The objective of the initial six months work was to formulate the experiment to judge the feasibility of the measurements and to define the appropriate experiments. The next year's work (12/74-11/75) will see the performance and analysis of the experiments themselves.

The fundamental premise of this work is that diffusion studies of the glass forming ion can be examined in zero-g environments and diffusion data obtained from these experiments will be unique because of earth based experimental problems.

Literature Background

The diffusion literature in glasses is most abundant and will be reviewed by reference to a relatively recent article by Williams[1] and the recent text by Doremus.[2] This literature contains little reference to diffusion of the glass forming ion doubtless as a consequence of the experimental difficulties of earth based experiments. The only work related to diffusion of the glass former which we have been able to locate is the work of Towers and Chipman[3] conducted in a blast furnace slag. These results indicated that the diffusion of silica appeared to occur by "something other than simple ion movement." This conclusion also

appears in the study of viscous flow of the silicate glasses where the activation energy for flow does not seem to be related to any simple model for the flow process. Unfortunately, the data obtained from these techniques is quite unreliable and exceedingly difficult to obtain.

Choice of System for Diffusion Studies

The criteria for selection of the appropriate system includes:

1. Relationship to "important" glass forming systems.
2. Availability of appropriate trace isotropes.
3. Processing limitations -- furnace temperature limits 1100^oC.
4. Diffusion times available for the experiment (4 to 6 minutes).

The system chosen for examination is the GeO_2-K_2O system which forms a glass up to 60 mole% K_2O and which theoretical calculations below indicate has highest diffusion coefficient of the alkali germanate family. The compositions chosen should have included the pure germania but temperature limitations preclude this choice. It was thus elected to examine three compositions and subsequently extrapolate from these glasses to the pure germania system. The three chosen include 7.5, 11.25 and 15 mole% K_2O which have liquidous temperatures low enough to allow an activation energy determination to be made in the range between their liquidous and 1100^oC.

Sample Definition

Table II indicates diffusion distances of the order of 0.0007 to 0.0025 inches ($\sqrt{Dt}$ for 1000 and 1100^oC) hence relatively small

diffusion samples are appropriate. The sample chamber[4] for the experimental rocket studies is to be 7/8 x 33/64 inch ID tube. This will accomodate three layers of samples 7/8 ÷ 3 or 0.2916 in (7.4 mm) long. Each layer will contain three cylindrical samples arrayed as shown in Figure 1 which will allow a maximum diameter of 0.276 in (7.01 mm). A total of three sample chambers will be required thus nine samples (3 each of 3 compositions) will be processed at each of three temperatures. Each of the 27 individual sample ampules will be individually sealed in a platinum capsule as shown in Figure 1b. Samples will be prepared by filling the ampule base with the appropriate glass composition then etching back to allow insertion of the top closure. The closure is to be sealed by fusion of the protruding upper lip with appropriate cooling of the sample chamber.

Processing

Lab Processing:

Glasses are to be prepared by melting of electronic grade GeO_2 with reagent grade K_2CO_3 in the platinum ampule. Furnace atmosphere is to be laboratory air with a temperature of at least 100°C above the liquidous for a minimum of one hour. Samples are to be annealed one hour at 25 to 50°C below the Littleton softening point then cooled to ambient.

The glass will be etched back into the ampule to allow insertion of the closure for sealing. The radiotracer[+] Ge 68 is to be painted on the exposed surface of the glass and dried. The

[+]Ge 68 from New England Nuclear in the form of HCl solution at February 1974 price of $260/milliCurie.

Figure 1a. Sample Arrangement.

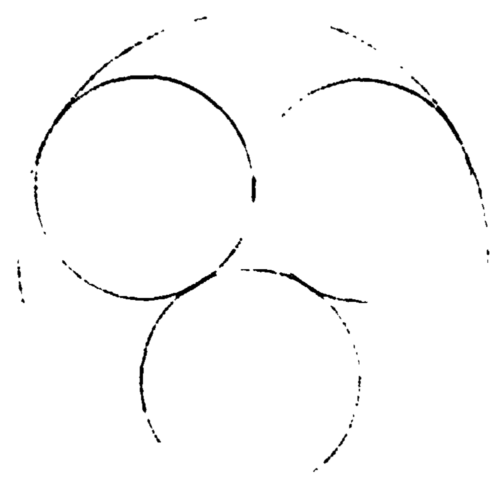
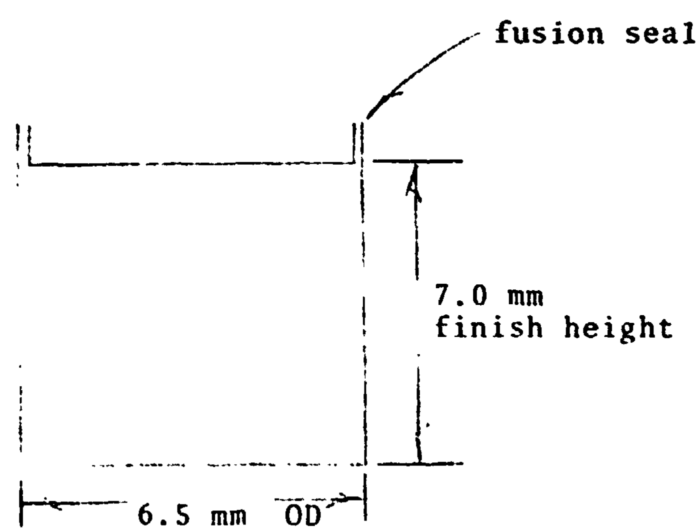


Figure 1b. Sample Ampule (0.1 mm - 0.010 in stock)



tracer deposit concentration is to be chosen such that a minimum activity in each anticipated diffusion slice is a minimum of 50 microCuries. The capsule is to be sealed using a microtorch with cooling as appropriate to minimize thermal effects on the glass sample.

The samples are to be enclosed in a sample capsule to be furnished by MSFC and sealed off with a helium atmosphere (pressure chosen to be such that one atmosphere is achieved at treatment temperature). The capsule and contents is then to undergo space processing.

Space Processing

The space processing of each capsule is to consist of a heating cycle designed to maximize time exposed to the diffusion temperature without exposing the low viscosity melt to gravitational forces. The cycles envisioned for each of the three different capsules is graphically depicted in Figure 2.

Post Processing Analysis

The post processing analysis is to consist of opening the sample ampules using an appropriate chemical machining solution. The diffusion profile is to be analyzed by etching the sample with appropriate reagents (to be developed) to remove a predetermined section thickness. The section contained in the solution is to be counted to determine the activity of each section.

Experimental Analysis

The appropriate solution to the diffusion equation for the present geometry is:

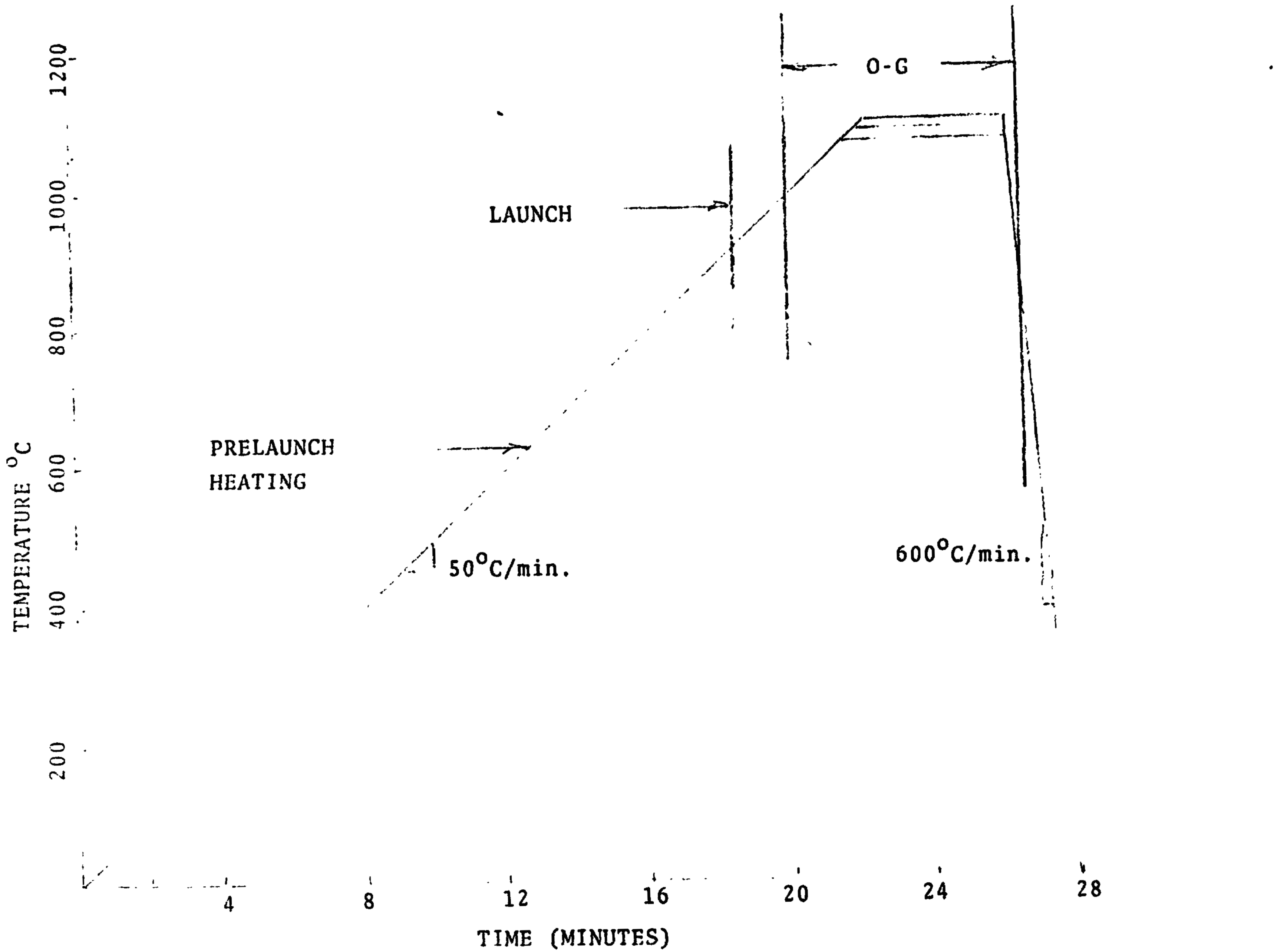


Figure 2. Space Processing Cycle.

$$c(x,t) = \frac{S}{\sqrt{\pi D_t t}} \ell^{-\frac{x^2}{4D_t t}}$$

where $c(x,t)$ is the concentration of radioactive atoms at a distance x from the initial face S is the initial total activity, t is the diffusion time and D_t is the diffusion coefficient at a temperature T. By examination it is apparent that a plot of ℓn $c(x)$ versus x^2 will be linear with a slope $- 1/4D_t t$ thence with a given time t one can obtain D_t from the slope of the ℓn $c(x)/x^2$ plot.

The diffusion coefficient in a liquid can be related to the viscosity of the liquid by the Nabarro-Herring equation

$$\eta = \frac{kT}{\alpha a_o D}$$

or by the Stokes-Einstein formula

$$\eta = \frac{kT}{6\pi a_o D}$$

where a_o is the diameter of the diffusing species.[5]

The validity of these expressions was examined by comparing the measured diffusion coefficient for silicon in a 39% CaO, 40% SiO_2, 21% Al_2O_3 slag,[3] with the viscosity of the slag. Unfortunately, the viscosity was not reported in the article, so the viscosity for a 38% Ca, 42% SiO_2, 20% Al_2O_3 slag was used; this paper gives the viscosities of a large number of slags of different ratios of $CaO:SiO_2:Al_2O_3$ and the viscosity does not change appreciably with composition around the composition of the slag in which

the diffusion coefficient was measured.

TABLE I

Slag Data[6]

$T(^{o}C)$	$D(x10^{8})^{2} cm^{2}/sec$	η poise
1350	3.7	46
1400	7.0	26
1450	13.5	16

Using $D = \dfrac{kT}{\alpha a_o \eta}$

$$1350^{o}C \qquad \alpha a_o = \frac{kT}{D\eta} = \frac{1.38x10^{-16}(1.62x10^{3})}{3.7 \times 10^{-8}(46)} = 13.1 \times 10^{-8} \text{ cm}$$

$$1400^{o}C \qquad \alpha a_o = \frac{1.38x10^{-16}(1.67x10^{3})}{7.0 \times 10^{-8}(26)} = 12.7 \times 10^{-8} \text{ cm}$$

$$1450^{o} \qquad \alpha a_o = \frac{1.38x10^{-16}(1.72x10^{3})}{13.5 \times 10^{-8}(16)} = 11.0 \times 10^{-8} \text{ cm}$$

if $a_o = 10^{-8}$ cm, $\alpha \simeq 12$

The Nabarro-Herring equations are:[7]

$$\eta = \left(\frac{3}{32\pi}\right)^{2/3} \frac{kT}{D\Omega_o} Vg^{2/3}$$

(Equal Quasi-spherical grains, No grain boundary flow)

$$\eta = \frac{1}{10} \left(\frac{3}{4\pi}\right)^{2/3} \frac{kT}{D\Omega_o} Vg^{2/3}$$

(Equal Quasi-spherical grains, tangential stress relaxes at the boundaries).

In our case, the "grain volume" Vg is the same as the volume of the mobile particle, so $Vg = \Omega_o = a_o^3$

$$\eta = \frac{1}{\alpha} \frac{kT}{Da_o}$$

from the first equation

$$\alpha = 1/\left(\frac{3}{32\pi}\right)^{2/3} = 10.4$$

and from the second

$$\alpha = 10/\left(\frac{3}{4\pi}\right)^{2/3} = 26.0$$

giving good agreement with the experimental value of $\alpha \approx 12$ and with the Stokes-Einstein formula where $\alpha = 6\pi = 18.8$.

A large compilation of viscosity data is given by Riebling[8] for binary germanates containing Li_2O, Na_2O, K_2O and Rb_2O. Using his Figure 3, the viscosity of a 4.29 mole% Na_2O melt at 993°C is 240 poise, therefore

$$D = \frac{kT}{\alpha a_o \eta} = \frac{1.38 \times 10^{-16} erg/^oK(1266^oK}{15(10^{-8} cm)\ (240\ poise)}$$

$$= 5 \times 10^{-9}\ cm^2/sec\ .$$

The following table is based on Reibling's viscosity data and the Nabarro-Herring equation with $\alpha = 15$.

TABLE II

Viscosity Data for Germania Glasses

Modifier	Mole %	T/°C	η(poise)	D Theoretical cm^2/sec	t=4 min $\sqrt{Dt}$ mils
Na_2O	4.29	1108	100	$1.3 \cdot 10^{-8}$	0.70
	7.79	1108	26	$4.9 \cdot 10^{-8}$	1.4
K_2O	7.5	1000	76	$1.5 \cdot 10^{-8}$	0.7
	11.25	1000	28	$4.2 \cdot 10^{-8}$	1.2
	15.0	1000	13	$9.0 \cdot 10^{-8}$	1.8
	7.5	1100	35	$3.6 \cdot 10^{-8}$	1.2
	11.25	1100	14.8	$8.5 \cdot 10^{-8}$	1.8
	15.0	1100	7.6	$1.9 \cdot 10^{-7}$	2.5

After Riebling[8]

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